



PATENT
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

Jean J. Frechet, *et al.*

Application No.: 09/963,858

Filed: September 25, 2001

For: DENDRIMERIC SUPPORT OR
CARRIER MACROMOLECULE

Customer No.: 43850

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Examiner: Riley, Jezia

Technology Center/Art Unit: 1637

DECLARATION OF PROFESSOR
FRECHET UNDER 37 C.F.R. § 1.132

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, Jean Frechet, Ph.D. declare as follows:

1. I am a Professor of Chemistry at the University of California at Berkeley. I have published over 200 scientific articles related to dendrimers and other dendritic polymers. My *Curriculum Vitae* is attached.
2. I am an inventor of the subject matter claimed in the U.S. Patent Application No. 09/963,858.
3. I have reviewed both the Office Action that issued May 24, 2004 and the references cited in this Office Action. The cited references are Magnusson, *et al.*, *Macromolecules*, **33**: 3099-3104 (2000) ("Magnusson"); Hult, *et al.*, (U.S. Pat. No. 5,418,301) ("Hult"); Trollsas, *et al.*, *Macromolecules*, **31**: 3439-3445 (1998) ("Trollsas"). I understand the content of these references.

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4. It is my understanding that the prior art cited in this case are all directed to “hyperbranched polymers”. The invention claimed in U.S. Patent App. No. 09/963,858 is directed to “dendrimers”. Therefore, I am submitting this declaration in order to illustrate the differences between “hyperbranched polymers” and “dendrimers”.

5. Polymers are often classified according to the degree of branching in their structures. The degree of branching (DB) is given by the following formula:

$$DB = \frac{D + T}{D + L + T}$$

wherein D , L , and T are the mole fractions of dendritic, linear, and terminal units. A degree of branching of zero connotes a linear polymer. Those polymers with a high DB value, approximately 0.3 or greater, are dendritic polymers.

6. Since there are several different ways that a molecule can exhibit a high degree of branching, there are several different types of dendritic polymers. Two members of the dendritic polymer family are “hyperbranched polymers” and “dendrimers”. Both of these terms have well-recognized meanings to those of skill in the art, as evidenced by an excerpt from a textbook that I have included as an exhibit (Exhibit A) attached to this declaration (PRINCIPLES OF POLYMERIZATION, George Odian, 4th Ed., Wiley-Interscience, 2004, pp. 174-195).

7. In “hyperbranched polymers”, the high degree of branching occurs in an uncontrolled, random manner. In fact, “hyperbranched polymers” are synonymously known in the art as “random hyperbranched polymers”, *see* Odian excerpt, p. 175. Hyperbranched polymers exhibit large variations in molecular shape and molecular weight, and typically possess DB values of between 0.3 to 0.7.

8. An example of a hyperbranched polymer structure is presented in Trollsas. An example of the structure of the polymer is shown in Scheme 2 on p. 3440. Please note that of the twelve monomers in this polymer, 2 monomers have no unreactive moieties (“dendritic” units; or D in the above formula); 7 monomers have some (in this case, one) unreactive moieties (“linear”

units; or L in the above formula); and 3 monomers possesses all (in this case, two) unreactive moieties ("terminal" units; or T in the above formula). This polymer from Trollsas has a DB value of 0.42, as shown below:

$$DB = \frac{2 + 3}{2 + 7 + 3} = 0.42$$

9. A DB value of 0.42 falls within the range of 0.3 and 0.7. Therefore, this polymer described by Trollsas is a "hyperbranched polymer".

10. An example of a hyperbranched polymer synthesis is also presented in Trollsas. The synthesis of the hyperbranched polymer described in the above paragraph is described in the last paragraph on page 3441. Please note that the polymer synthesis took place in one step and in one pot. A 'one-step, one pot' synthesis is a characteristic of a hyperbranched polymer.

11. Because of their method of preparation, a hyperbranched polymer cannot have a DB of 0.9-1.0.

12. In "dendrimers", the high degree of branching occurs in a controlled, planned manner. Dendrimers are synthesized in multiple successive reaction and purification steps with one layer added at a time. These conditions of synthesis produce molecules that have generations (*i.e.* distinct layers), which are analogous to the layers of an onion. Dendrimers therefore have highly regular, globular shapes. In addition, dendrimers exhibit narrow variations in molecular shape and molecular weight, and can possess DB values of between 0.9 to 1.0. When I publish my research on dendrimers, the DB value is 1, unless otherwise noted.

13. An example of a dendrimer structure is presented at the bottom of FIG. 1 of the instant application (U.S. Patent Application No. 09/963,858). In FIG. 1, please note that all of the monomers in this polymer are reacted. This complete, or near complete, monomer reactivity leads to the characteristic DB values which are between 0.9 and 1.0. In the case of the dendrimer shown in Figure 1, the molecule has 21 "Dendritic" units, 24 "Terminal" units and no "Linear" units. Therefore the DB value of this polymer is 1.0 as shown below:

$$DB = \frac{21 + 24}{21 + 0 + 24} = 1.0$$

14. Based on this DB value, this polymer is classified as a dendrimer.
15. An example of a dendrimer synthesis is also presented in the instant application. The synthesis of the dendrimer described in paragraph 13 is described in Example 2. Please note that the dendrimer synthesis takes place in sequential steps involving generation growth (addition of chemically protected monomers), then purification, then removal of the protecting groups from the monomers, and so on as necessary. Through these steps, 6 generations, or layers, are attached to the dendrimer core. This sequential step synthesis, with a purification step following the generation growth step, is a characteristic of a dendrimer.
16. There are three references which have been cited as prior art against my application: Magnusson, *et al.*, *Macromolecules*, **33**: 3099-3104 (2000) ("Magnusson"); Hult, *et al.*, (U.S. Pat. No. 5,418,301) ("Hult"); Trollsas, *et al.*, *Macromolecules*, **31**: 3439-3445 (1998) ("Trollsas"). I have read, and I understand, each of these three references. Each of the three references cited in this Office Action describe "random hyperbranched polymers", rather than the "dendrimers" of my invention.
17. The polymers of Magnusson are hyperbranched polymers, rather than dendrimers. This is evident from the DB values of the polymers, which are described in the Abstract of the paper. Polymers of Magnusson have DB values of 0.47 (*see*, Abstract). This DB value is indicative of hyperbranched polymers, not dendrimers.
18. The polymers of Trollsas are also hyperbranched polymers, and not dendrimers. This is evident from the DB values of the polymers, which are calculated above as 0.42 and described in Figure 4 on p. 3444 of Trollsas as 0.37 and 0.46. These DB values are indicative of hyperbranched polymers, not dendrimers.
19. The Hult patent (U.S. Patent No. 5,418,301) deserves a special discussion. This is due to Hult's occasional use of "dendrimers" in a "hyperbranched polymer" patent.

20. Hult is directed to “hyperbranched polymers”. The entire specification is directed to the discussion of “hyperbranched polymers”. All 52 Examples in Hult describe “hyperbranched polymers”. However, at several points, Hult refers to its “hyperbranched polymers” as “dendrimers”. Hult’s usage of “dendrimers” is discussed below.

21. In FIG. 1 of Hult, a polymer structure is presented. This polymer is constructed in two steps. In the first, “growth” step, the polymer is grown to produce what Hult describes as a “1.5 generation dendrimer” [Column 7, lines 58-64]. The structure of this “1.5 generation dendrimer” is presented in the middle of FIG. 1. In the second “chain stopper” step, the polymer is terminated with lauric acid. The structure of this capped polymer is presented in the bottom of FIG. 1.

22. Please note that what Hult describes as a “1.5 dendrimer” has 2 Dendritic units, 4 Linear units, and 4 Terminal units. Therefore the DB value of this polymer is 0.6 as shown below:

$$DB = \frac{2 + 4}{2 + 4 + 4} = 0.6$$

23. Based on this DB value, the Hult polymer in FIG. 1 is actually a “hyperbranched polymer”, and not a “dendrimer”.

24. In FIG. 2 of Hult, a hypothetical dendrimer synthesis involving hydroxyl groups (A) and carboxylic acid groups (B) is presented. These groups are further described in column 2, lines 8-30. However, no reaction conditions, either actual or prophetic, are presented for producing a polymer with a DB of between 0.9 and 1.0. In addition, no purification steps are described in the syntheses, even though this a requirement for proper dendrimer growth. Since these disclosures in Hult are missing these two important pieces, these disclosures do not disclose dendrimers.

25. As mentioned in paragraph 20, all 52 Examples in Hult are directed to “hyperbranched polymers”. Example 51 is presented in Hult as describing a “9-generation

dendrimer”, but this is a misnomer. As mentioned earlier, dendrimer synthesis requires a purification step after the generation growth step. In Example 51, on the other hand, Hult presents a typical batchwise addition process where a portion of dimethylolpropionic acid and para-toluene sulphonic acid are added, then heated, then placed under vacuum to remove the water that has formed during the reaction. Then, in the same flask and without purification of the product, another portion of reactants is added and the cycle starts anew. Since Example 51 does not involve sequential generation growth and purification steps, Example 51 of Hult does not describe dendrimer synthesis.

26. The only other references to “dendrimers” in Hult conflict with each other. In column 1, lines 22-25, Hult describes a dendrimer publication (Tomalia *et al.*, *Angew. Chem. Int. Ed. Engl.*, 138-175 (1990)). Hult then states,

Products quite different from the present invention are in said publication described (Tamalia) [sic], which publication (Tamalia) [sic] discloses the preparation of polyamide amines of the dendrimer type . . . the present invention refers to a dendritic, that is a hyperbranched, macromolecule of the polyester type.

Hult, column 1, lines 25-35

In this passage, Hult is stating that dendrimers are not encompassed in this invention.

27. In the next column, column 2, lines 8-11, Hult mentions that “. . . a hyperbranched macromolecule of the dendrimer type has been brought about.” This statement is in conflict with Hult’s column 1 assertion that dendrimers are not encompassed in this invention. This statement is also in conflict with art-recognized definitions, since it is impossible for a polymer to simultaneously be a “hyperbranched polymer” (DB values of 0.3-0.7) and a “dendrimer” (DB values of 0.9-1.0).

28. As shown above, although the word “dendrimer” is used in Hult, it is a) incorrectly used to describe a “hyperbranched polymer”; b) incorrectly used to describe a synthesis that does not possess purification steps; c) specifically disavowed as part of the

invention; and d) described as being part of equivalent to a hyperbranched polymer, which is not possible.

29. Since the invention in Hult is a hyperbranched polymer, and none of Hult's uses of the word "dendrimer" actually describe a dendrimer, Hult is a hyperbranched polymer invention.

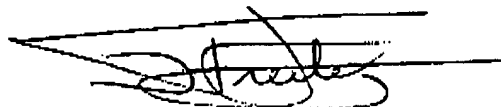
30. Additional corroboration for Hult's use of hyperbranched polymers is in the DB values for the polymers described in this patent. While the DB values of the polymers are not provided in the patent publication itself, Hult's subsequent scientific publications have disclosed the DB values of these polymers. In one of these publications, entitled "Hyperbranched Aliphatic Polyesters" (Malmstrom *et al.*, *Macromolecules*, **28**: 1698-1703 (1995)) and enclosed with this declaration, the DB value of these polymers is 0.80. This DB value was later found to be in error due to interactions between the hyperbranched polymers and the NMR solvent acetone. The DB value was later revised downward to 0.50 in a subsequent paper, (Malmstrom *et al.*, *Polymeric Materials Science and Engineering*, **77**: 151-152 (1997)), which is also enclosed. The corrected DB value is within the range for "hyperbranched polymers."

31. Therefore, based upon the discussion above, it is my opinion that the polymers described by Trollsas, Magnusson, and Hult are hyperbranched polymers, and not dendrimers.

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32. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Dated: Nov 19, 2004



Jean Frechet, Ph.D.

PRINCIPLES OF POLYMERIZATION

Fourth Edition

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1 INTRODUCTION

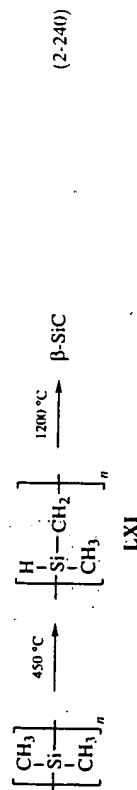
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pressures locally for short bursts [Kim and Matyjaszewski, 1988]. The mechanism for this reaction is not established, but most evidence indicates polymerization is a complex process involving some combination of radical, anionic, and silylene (the Si analog of carbene) intermediates [Gauthier and Worsfold, 1989; Matyjaszewski et al., 1988]. Furthermore, although included in this chapter, the polymerization is probably a chain reaction. It is included here because of its technological importance in complementing the sol-gel process for producing ceramics. The corresponding polystannanes and polygermanes (Sn and Ge in place of Si) have also been synthesized by the Wurtz coupling reaction.

Polysilanes have been synthesized with various combinations of alkyl and aryl substituents. Polysilanes, such as polydimethylsilane or polydiphenylsilane, with symmetric substitution are highly crystalline and show little or no solubility in a range of organic solvents. (The IUPAC names of the two polymers are poly(dimethylsilane) and poly(diphenylsilane), respectively. They have also been referred to as *polydimethylsilylene* and *polydiphenylsilylene*.) Crystallinity is decreased and solubility increased when R and R' are different or for copolymers derived from two different symmetrically substituted dichlorosilanes. There is considerable interest in polysilanes from several viewpoints. Many of the interesting properties of polysilanes result from the relative ease of delocalization of the electrons in the catenated Si-Si σ -bonds as evidenced by the strong ultraviolet absorption at 300–400 nm. Polysilanes undergo photolytic radical cleavage with a high quantum yield and offer potential as radical initiators and positive photoresists. (In a positive photoresist application, the portions of a polymer not protected by a mask are degraded by irradiation and then dissolved by solvent or photovolatilized.) Polysilanes also offer potential as semiconductor, photoconductor and nonlinear optical materials.

The greatest interest in polysilanes is probably in their use as *preceramic polymers*. The normal powder metallurgy techniques for processing ceramic materials limits the complexity of the objects that can be produced. Polysilane chemistry offers an alternate with good potential for making a variety of objects, including fiber. Thermolysis of a polysilane in an inert atmosphere at 450°C yields a polycarbosilane through a complex rearrangement process. For example, poly(dimethylsilane) yields poly(methylsilanediylmethylene) (LXI) (Eq. 2-240). A soluble portion of the polycarbosilane is isolated by fractional precipitation from *n*-hexane and used as a ceramic precursor. The soluble polycarbosilane can be formed into objects (including fibers) and then pyrolyzed at 1200°C to yield the corresponding crystalline β -silicon carbide ceramic objects. Other organometallic polymers are being studied for use as precursor polymers for other ceramic systems, such as polysilazanes for silicon nitride [Baldus and Jansen, 1997; Baney and Chandra, 1988].



The use of a monoalkylchlorosilane in the Wurtz-type polymerization is reported to yield (RSi)_n, referred to as polyalkylsilylene [Bianconi et al., 1989]. The elemental composition and NMR spectra of the polymer suggest a three-dimensional crosslinked structure.

2-16 DENDRITIC (HIGHLY BRANCHED) POLYMERS

There is an ongoing effort to synthesize different, well-defined polymer architectures. A considerable thrust in this direction has been the synthesis of *dendritic* polymers [Bosman et al.,

1999; Fischer and Vogtle, 1999; Frechet and Tomalia, 2002; Kim, 1998; Newkome et al., 1999, 2001; Tomalia, 2001; Tomalia et al., 1990; Vogtle et al., 2000; Voit, 2000]. Dendritic polymers are highly branched polymers—polymers with treelike branching, where there are branches on branches on branches, and so on. Dendritic polymers differ considerably from linear (and also from lightly branched) polymers in their molecular shapes. Dendritic polymers have globular shapes, whereas linear polymers have elongated shapes. The term *globular shape* indicates that the dimensions of the polymer molecule are about the same in all directions, whereas the term *elongated shape* indicates that the dimensions are much greater in one direction than the other directions. [In the extreme, the globular shape is illustrated by a sphere or ellipsoid (where no axis is much longer than the other axes) and the elongated shape, by a cylinder (where the length of the cylinder is much greater than the diameter).]

The difference in molecular shape leads to differences in the attractive secondary forces present in linear and dendritic polymer molecules. The attractive secondary forces are greater for linear (elongated) polymers because the molecules pack together and attract each other over a larger surface area than is possible for dendritic (globular) polymer molecules. Also, dendritic polymer molecules do not undergo chain entanglements as do linear polymers. Thus, unlike linear polymers, dendritic polymers rarely have sufficient strength to be useful as fibers, rubbers, and plastics. However, because of their low secondary forces, dendritic polymers have higher solubility and miscibility with other materials, including other polymers. The globular shape of dendritic polymers also results in lower hydrodynamic volume and lower viscosity compared to linear polymers. Dendritic polymers have potential for use as additives to polymers and oils to modify their viscosity, melt behavior, and lubricating properties; and to aid in compatibilizing mixtures of different materials. The difference between linear and dendritic polymers has an analogy in nature. For example, there are globular and elongated (more often called *fibrous*) proteins. The fibrous proteins have strong secondary attractive forces and are used to construct such materials as bone, skin, and nails. Globular protein molecules do not attract each other strongly and are soluble in aqueous media, and this fits their biological functions. Globular proteins perform catalytic, transport, regulatory, hormonal, and other functions that require their solubility in blood and the other aqueous media of cells and tissues.

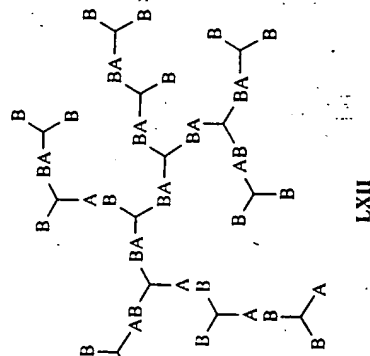
Another (obvious) difference between linear and dendritic polymers is that dendritic polymers have a much larger number of chain ends. The interesting situation arises when the dendritic polymers are synthesized by methods that result in functional groups such as NH₂, OH, or COOH at the chain ends. Such polymers carry a large number of derivatizable functional groups and hold promise as carrier molecules for drug delivery, gene therapy, catalysis, and sensors [Frechet and Tomalia, 2002; Stiriba et al., 2002].

Two types of dendritic polymers have been developed: hyperbranched polymers and dendrimers.

2-16a Random Hyperbranched Polymers

Hyperbranched polymers are produced in a one-pot synthesis using a multifunctional monomer such as AB_f where *f* is 2 or greater [Bolton and Wooley, 2002; Galina et al., 2002; Kim, 1998; Voit, 2000]. Hyperbranched polymers are more correctly called *random hyperbranched* polymers because the branching occurs in a random manner. For an AB₂ multifunctional monomer such as a diamino or dihydroxy carboxylic acid, *f* = 2 and the product has a structure described by LXII. With increasing conversion AB₂ adds to LXII to produce higher \bar{X}_n polymer. The random hyperbranched polymer at every stage of its growth has a single

unreacted A group. The number of unreacted B groups is given by Eq. 2-241 [Kim, 1998]. LXII has $\bar{X}_n = 13$ and 14 unreacted B groups. The number of unreacted B groups increases with increasing \bar{X}_n and f .



$$\text{Unreacted B groups} = [1 + \bar{X}_n(f - 1)] \quad (2-241)$$

A hyperbranched polymer is often characterized by the degree of branching DB [Holter et al., 1997; Jo and Lee, 2001; Kim, 1998; Lee et al., 2000]. For the hyperbranched polymer produced from AB_2 , there are three different types of repeat units: dendritic, linear, and terminal units defined as units having two, one, and no B groups reacted, respectively. The degree (fraction) of branching (DB) is given by

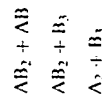
$$DB = \frac{D + T}{D + T + L} \quad (2-242)$$

where D , L , and T are the mole fractions of dendritic, linear, and terminal units. For high molecular weight polymers, D , L , and T have limiting values of 0.25, 0.25, and 0.50, respectively, and DB is 0.50. (For linear polymers, DB is zero. DB is 1 for dendrimers—Sec. 2-16b.)

Hyperbranched polymers are similar to linear polymers in that they show molecular weight polydispersity. There is also polydispersity due to constitutional isomerism, resulting from the different placements of monomer units. For example, LXII has many isomers, such as those arising from placement of the lower leftmost AB_2 unit at any of the other positions around the perimeter of the molecule. The synthesis of hyperbranched polymers has inherent difficulties which limit molecular weight or shape. One is the occurrence of intramolecular cyclization, which decreases the functional groups available for polymerization. Another difficulty is the steric crowding that occurs within and/or at the periphery of hyperbranched molecules with increasing conversion and molecular size. (This steric crowding effect, discussed extensively for dendrimers, is called *de Gennes dense packing* [de Gennes and Hervet, 1983].) Although steric crowding may not limit polymer molecular weight (as it does for dendrimers), it will affect molecular shape. Functional groups in some regions become inaccessible for reaction, but growth proceeds in other regions where functional groups are accessible. Steric crowding in a region is relieved by an increase of linear (one unreacted

B group) units and fewer dendritic (no unreacted B groups) units. The polydispersity in molecular weight and isomerism, the intramolecular cyclization, and the molecular shape variations due to steric crowding contribute to the random nature of hyperbranched polymers.

Hyperbranched polymers can also be synthesized from the following systems [Jikei and Kakimoto, 2001]:



The $AB_2 + AB$ system is equivalent to AB_2 except that AB_2 units are separated from each other by AB units. The $AB_2 + B_3$ system modifies the AB_2 system by using B_3 as a central core from which polymerization radiates and offers greater control of molecular shape. The $A_2 + B_3$ system is one of the standard systems used to produce crosslinked polymers (Sec. 2-10). It is useful for synthesizing hyperbranched polymers only when crosslinking is minimized by limiting conversion and/or diluting the reactants with solvent.

Hyperbranched polymers can also be synthesized by chain polymerization, ring-opening polymerization, and combinations of ring-opening and step polymerization [Kim, 1998; Voit, 2000] (Secs. 3-6c, 3-15b-4, 3-15b-5, 3-15c, 5-4c).

2-16b Dendrimers

Dendrimers are dendritic (highly branched) polymers with a more controlled structure than the hyperbranched polymers [Bosman et al., 1999; Fischer and Vogtle, 1999; Grayson and Fréchet, 2001; Hecht, 2003; Newkome et al., 1999; Simanek and Gonzalez, 2002; Tomalia, 2001; Tomalia and Fréchet, 2002; Vogtle et al., 2000]. Other terms have also been used to describe various dendritic polymers—*arboral*, *cascade*, *cauliflower*, *starburst*. The synthesis of dendrimers differs greatly from the one-pot process for hyperbranched polymers. Dendrimers are synthesized by more complicated processes involving sequential reactions. There are two different methods: divergent and convergent. The *divergent* method starts with a core molecule and builds outward by attaching to the core successive layers (or generations) of monomer units one at a time. A large variety of reactions (organometallic as well as organic) have been used in synthesizing dendrimers.

The divergent method is illustrated in Fig. 2-22 for the synthesis of polyamidoamine (PAMAM) dendrimers [Tomalia et al., 1990]. A repetitive sequence of two reactions are used—the Michael addition of an amine to an α,β -unsaturated ester followed by nucleophilic substitution of ester by amine. Ammonia is the starting core molecule. The first step involves reaction of ammonia with excess methyl acrylate (MA) to form LXIII followed by reaction with excess ethylenediamine (EDA) to yield LXIV. LXV is a schematic representation of the dendrimer formed after four more repetitive sequences of MA and EDA.

Dendrimers are characterized by the number of *generations*, the number of layers or shells of repeat units, analogous to the layering of an onion. The number of generations is the number of repetitive sequences of the Michael addition and nucleophilic substitution reactions. LXIV and LXV correspond to generations 1 and 5, respectively. LXIV has three arms or three NH_2 groups. Each generation doubles the number of arms or NH_2 groups. The fifth-generation dendrimer (LXV) has 48 arms or NH_2 groups.

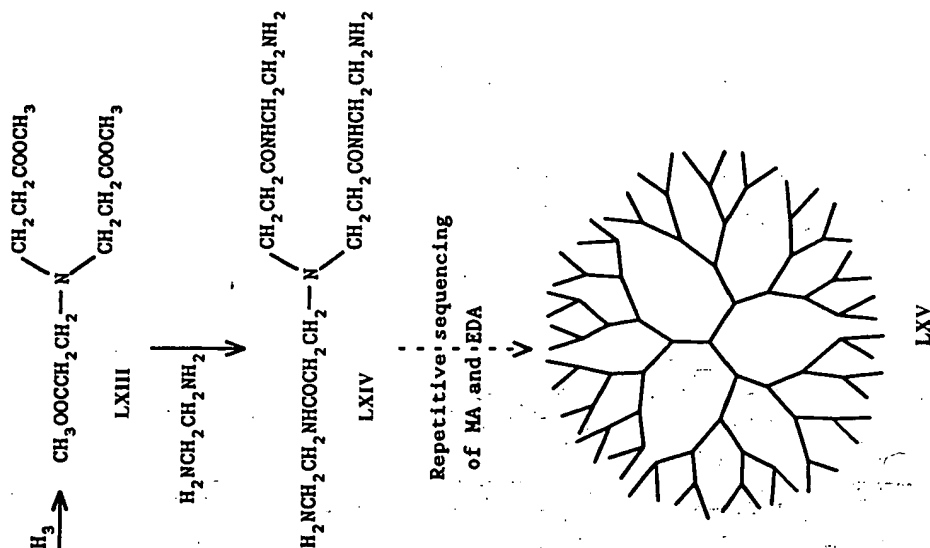


Fig. 2-22 Divergent synthesis of PAMAM dendrimer. Generation is 1 for LXIV and 5 for LXV.

The *convergent* method of dendrimer synthesis is shown in Fig. 2-23 for a dendrimer of five generations. Dendrimeric fragments are synthesized by repetitive reactions, and then several (three for the dendrimer in Fig. 2-23) are joined together in the last step by using a central core molecule to form the dendrimer. The method requires the use of appropriate reactants and chemical reactions. The functional group Z has an identity such that smaller fragments can be linked together to form a larger fragment, either by direct reaction with each other or with a coupling agent. The larger fragment must also have a Z group because of the choice of appropriate reactants or coupling agent, and the linking of fragments continues in a repetitive manner. In some systems Z is a protected functional group that is deprotected at the appropriate time.

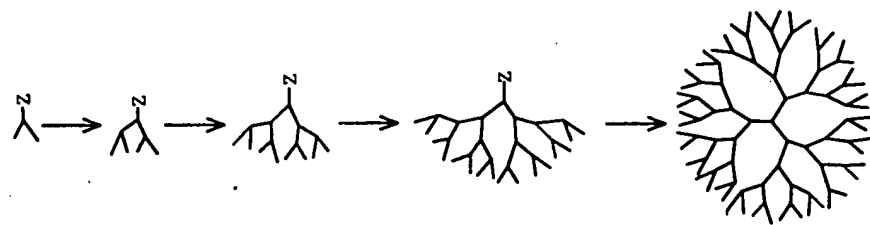


Fig. 2-23 Convergent synthesis of dendrimer.

The convergent method also allows the synthesis of dendrimers of regular shapes other than spheres. Ellipsoid- and rod-shaped dendrimers can be synthesized by using appropriate core molecules [Tomalia, 2001].

Dendrimers have the potential for greater structural regularity and narrower molecular weight distribution than hyperbranched polymers. However, there are problems inherent in dendrimer synthesis that must be controlled to achieve this potential. There are many reactions to carry out, and each reaction includes physical manipulations to wash the product free of reagents. Each of these reactions and physical manipulations must be carried out with 100% efficiency to achieve a monodisperse product. For example, if a fraction of the second generation dendrimer is not perfect, that is, if some functional groups are unreacted, this imperfection is carried through each subsequent generation, and new imperfections in subsequent generations accumulate and carry forward to the higher generations. This is less of a problem for the convergent method than for the divergent method since the latter requires the

carrying out of a much greater number of reactions on a single molecule. The application of solid-phase synthetic techniques (Sec. 9-14) appears useful for increasing the efficiency of dendrimer synthesis [Lebreton et al., 2001].

It becomes progressively more difficult to form each new generation in the divergent synthetic method because of the de Gennes dense packing effect. The steric crowding within a dendrimer molecule and among its peripheral functional groups increases progressively for higher-generation dendrimers. This results in structural defects by distorting the shape of the dendrimer molecule and preventing complete reaction of all functional groups. Steric crowding becomes quite significant after about five generations, and the purity of higher-generation dendrimers decreases fairly rapidly. There are very few reports of dendrimers containing more than 10-15 generations. Steric crowding would appear at first glance to be not as important in the convergent synthetic method because the dendrimer fragments are relatively small compared to the dendrimer molecule. However, steric crowding is present when a number of dendrimer fragments (e.g., three for the synthesis described in Fig. 2-23) need to be joined together by reaction with a central core molecule to form the dendrimer. The steric crowding can be relieved by using a larger and more flexible central core molecule.

How do dendrimers and hyperbranched polymers compare from an industrial viewpoint? Dendrimers offer the potential for producing polymers whose molecular size and structure are more regular and less polydisperse. Hyperbranched polymers are easier and cheaper to synthesize—a one-pot synthesis compared to the multipot synthesis for dendrimers. However, not too many AB_n monomers are readily available, and this may modify the overall economics. Hyperbranched polymers will probably find use in larger-scale or commodity applications where lower cost is a necessity and dendrimers in specialty applications where higher cost is justified.

2-17 MISCELLANEOUS TOPICS

2-17a Enzymatic Polymerizations

2-17a-1 In Vivo (within Living Cells)

Plants and animals synthesize a number of polymers (e.g., polysaccharides, proteins, nucleic acids) by reactions that almost always require a catalyst. The catalysts present in living systems are usually proteins and are called *enzymes*. Reactions catalyzed by enzymes are called *enzymatic reactions*; polymerizations catalyzed by enzymes are *enzymatic polymerizations*. Humans benefit from naturally occurring polymers in many ways. Our plant and animal foodstuffs consist of these polymers as well as nonpolymeric materials (e.g., sugar, vitamins, minerals). We use the polysaccharide cellulose (wood) to build homes and other structures and to produce paper.

Various microorganisms, such as yeast and bacteria, have been used in industrial bioreactors to produce a host of important products, including alcoholic beverages, penicillin, and carbohydrates (including polysaccharides such as starch). More recently, proteins have been produced for therapeutic purposes by *recombinant DNA technology* [Blei and Odian, 2000]. Diabetics who lack insulin have until now taken insulin derived from other animals such as pigs and beef. Pig and beef insulins are close to but not exactly the same in structure as human insulin. The bacterium *Escherichia coli* has been used to produce human insulin by recombinant DNA technology. The bacterial DNA is altered in the laboratory to contain the gene for human insulin and then inserted into the organism by various techniques

(chemical or thermal shock, viral vectors, microinjection). The *E. coli* are fooled into using the altered DNA to produce the desired human protein. The protein is then harvested by breaking the bacterial cell walls and using an appropriate separation technique. This approach offers much potential for producing a host of therapeutic proteins.

There has been an effort to use microorganisms to produce commodity polymers for use as plastics, elastomers, and fibers as a supplement to the polymers produced by the traditional methods such as those described throughout this chapter. Some species of bacteria produce poly(hydroxyalkanoate) (PHA) storage (reserve) polymers when growth is restricted by some nutrient other than their carbon-containing food source [Jung et al., 2000; Shah et al., 2000]. This is analogous to the storage in higher animals of carbohydrates and lipids as glycogen and triacylglycerols, respectively [Blei and Odian, 2000]. Bacterial cultures such as *Pseudomonas oleovorans* and *Ralstonia eutrophia* have been used to produce PHA polymers in the laboratory. The polyester structure can be varied to some extent by controlling the organic feed. *Biopol* is a small-scale commercial product—a copolymer of 3-hydroxybutanoate and 3-hydroxypentanoate repeat units. Such polymers are of interest because they are environmentally degradable and offer an alternative to recycling the large volumes of nondegradable polymer wastes.

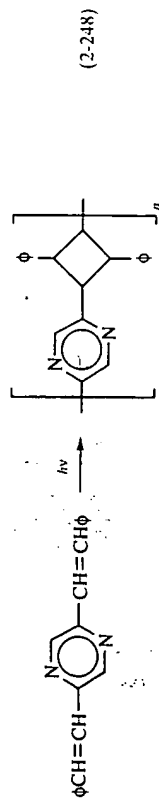
The mechanism for bacterial synthesis of PHA is not the simple dehydration reaction between alcohol and carboxyl groups. It is more complicated and involves the coenzyme A thioester derivative of the hydroxyalkanoic acid monomer (produced from the organic feedstock available to the bacteria) [Kamachi et al., 2001]. Growth involves an acyl transfer reaction catalyzed by the enzyme *PHA synthase* (also called a *polymerase*) [Blei and Odian, 2000]. The reaction is not a step polymerization but is a chain polymerization with the characteristics of a living polymerization [Su et al., 2000] (Secs. 3-15, 5-2g, Chap. 7).

2-17a-2 In Vitro (outside Living Cells)

The *in vivo* production of commodity polymers has been limited by the difficulties of controlling these processes, including the control of the reaction conditions required to maintain a bacterial culture and the conditions needed to harvest the polymer product. In addition, the *in vivo* method, although applicable for a few polymers, is not useful for the full range of polymers produced by the typical chemical processes. An alternate to the *in vivo* method is the use of enzymes to catalyze *in vitro* polymerizations. *In vitro enzymatic polymerizations* are enzyme-catalyzed polymerizations taking place outside cells, that is, taking place in glass and metal reactors. Biochemists carry out *in vitro* enzymatic polymerizations using the same reactants present in living cells for the purpose of understanding the reactions within living cells [Kamachi et al., 2001]. For polymer chemists, the major effort is the use of enzymes extracted from living cells to carry out *in vitro* polymerizations of nonnatural substrates to produce polymers for industrial use [Gross et al., 2001; Kobayashi, 1999; Kobayashi et al., 2001].

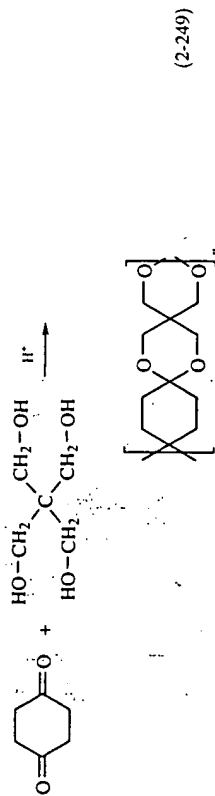
Lipases are enzymes that catalyze the *in vivo* hydrolysis of lipids such as triacylglycerols. Lipases are not used in biological systems for ester synthesis, presumably because the large amounts of water present preclude ester formation due to the law of mass action which favors hydrolysis. A different pathway (using the coenzyme A thioester of a carboxylic acid and the enzyme *synthase* [Blei and Odian, 2000]) is present in biological systems for ester formation. However, lipases do catalyze the *in vitro* esterification reaction and have been used to synthesize polyesters. The reaction between alcohols and carboxylic acids occurs in organic solvents where the absence of water favors esterification. However, water is a by-product and must be removed efficiently to maximize conversions and molecular weights.

(Eq. 2-248) [Braun and Wegner, 1983; Hasegawa et al., 1988, 1998]. This polymerization is a solid-state reaction involving irradiation of crystalline monomer with ultraviolet or ionizing radiation. The reaction is a *topochemical* or *lattice-controlled* polymerization in which reaction proceeds either inside the monomer crystal or at defect sites where the product structure and symmetry are controlled by the packing of monomer in the lattice or at defect sites, respectively.



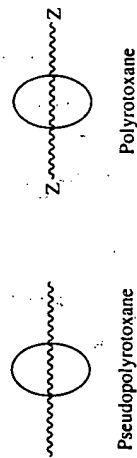
2-17d Spiro Polymers

Polymer chains based on *spiro structures* have been studied as another route to heat-resistant polymers [Kurita et al., 1979]. A spiro structure is a double-strand structure (Sec. 1-2c) in which the uninterrupted sequence of rings have one atom in common between adjacent rings. (Adjacent rings in ladder polymers have two or more atoms in common.) An example of a spiro polymer is the polyspiroketal synthesized from 1,4-cyclohexanedione and pentaerythritol (Eq. 2-249). The low solubility and intractability of spiro polymers makes it difficult to synthesize or utilize high-molecular-weight polymers.



2-17e Pseudopolyrotaxanes and Polyrotaxanes

Pseudopolyrotaxanes and *polyrotaxanes* are polymers composed of a linear polymer chain threaded through one or more cyclic species [Gibson and Mahan, 2000; Raymo and Stoddart, 1999]. Synthesis of pseudopolyrotaxanes and polyrotaxanes involves polymerization of monomer(s) in the presence of the cyclic species. Cyclodextrins, crown ethers, paracyclophane, and other macrocycles are used as the cyclic component. Both step and chain polymerizations have been successfully used.



There is a statistical extent of threading of the linear polymer chain through the macrocycles present in the reaction system. The extent of threading is greater for larger macrocycles. Threading is reversible and is dependent on enthalpic and entropic factors. The difference between pseudopolyrotaxanes and polyrotaxanes is the placement of bulky groups (Z), referred to as *stoppers*, along the linear polymer for polyrotaxanes. The stoppers prevent unthreading of the macrocycles from the linear polymer chain.

There are many variations on the structures possible for polyrotaxanes. One variation is the number of macrocycles per linear polymer chain. Another is the placement of the stopper groups. One may have stopper groups only at the two chain ends of the polymer. Alternately, there may be many stopper groups distributed randomly along the polymer chain between different cyclic species. In step polymerization, one may achieve the first situation by adding a reactant with the stopper groups at the end of the polymerization—to end-cap the linear polymer. The second situation can be achieved by including a monomer with stopper groups as part of the reaction system at the beginning of polymerization. In chain polymerization, the two different situations can be achieved by using appropriate initiators and terminating agents, or monomers containing the stopper groups.

Another variation for both pseudopolyrotaxanes and polyrotaxanes is the placement of the cyclic component on linear side chains during a graft polymerization process.

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